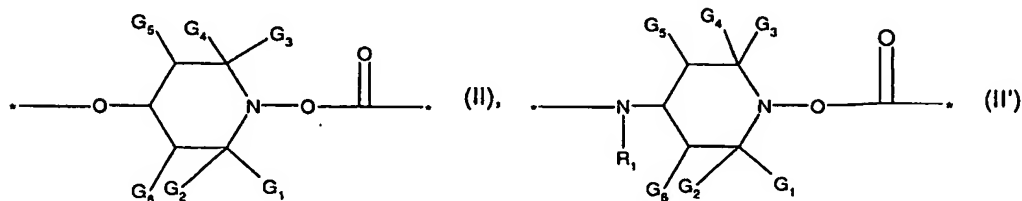
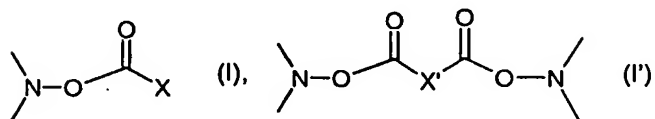


Claims

1. A flame retardant composition which comprises

- (a) a thermoplastic polymeric substrate,
- (b) a mixture of
 - (i) a hydroxylamine ester having a structural element of formula (I) or formula (I') or a polymeric hydroxylamine ester having a repetitive structural unit of formula (II) or (II')



wherein

X is hydrogen, C₁-C₃₆alkyl, C₂-C₃₆alkenyl, C₂-C₁₈alkinyl, C₆-C₁₀aryl, -O-C₁-C₁₈alkyl, -O-C₆-C₁₀aryl, -NH-C₁-C₁₈alkyl, -NH-C₆-C₁₀aryl, -N(C₁-C₆alkyl)₂ ;

X' is a direct bond or C₁-C₃₆alkylene, C₂-C₃₆alkenylene, C₂-C₃₆alkinylene, -(C₁-C₆alkylene)-phenylene-(C₁-C₆alkylene)- or a group from a dimer acid;

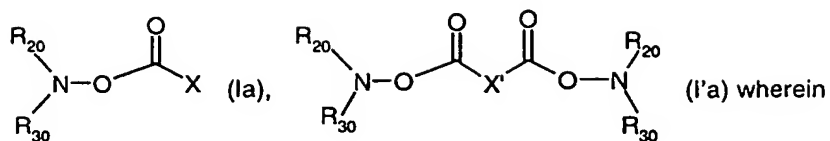
G₁, G₂, G₃ and G₄ are independently alkyl of 1 to 4 carbon atoms, or G₁ and G₂ together and G₃ and G₄ together, or G₁ and G₂ together or G₃ and G₄ together are pentamethylene;

G₅ and G₆ are independently hydrogen or C₁-C₄ alkyl;

R₁ is C₁-C₁₂alkyl, C₅-C₇cycloalkyl, C₇-C₉aralkyl, C₂-C₁₈alkanoyl, C₃-C₅alkenoyl or benzoyl; and

(ii) a flame retardant compound selected from the group consisting of halogenated, phosphorus, boron, silicon and antimony compounds, metal hydroxides, metal hydrates, metal oxides and mixtures thereof.

2. A composition according to claim 1 wherein the hydroxylamine ester is of formula (Ia) or (I'a)



X is hydrogen, C_1-C_{36} alkyl, C_2-C_{36} alkenyl, C_2-C_{18} alkinyl, C_6-C_{10} aryl, $-O-C_1-C_{18}$ alkyl, $-O-C_6-C_{10}$ aryl, $-NH-C_1-C_{18}$ alkyl, $-NH-C_6-C_{10}$ aryl, $-N(C_1-C_6alkyl)_2$;

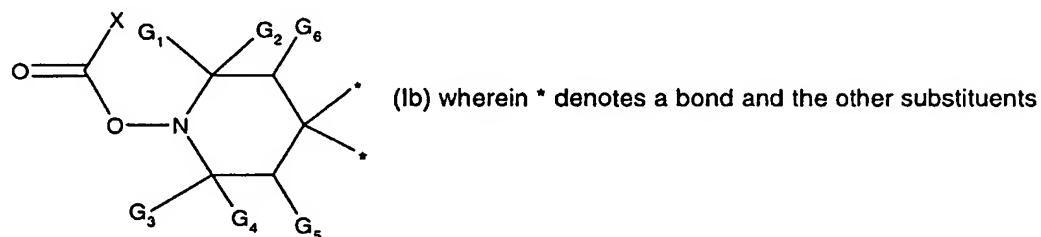
X' is a direct bond or C_1-C_{36} alkylene, C_3-C_{36} alkenylene, C_3-C_{36} alkinylene, $-(C_1-C_6alkylene)-phenyl-(C_1-C_6alkylene)$ or a group from a dimer acid;

R_{20} and R_{30} independently are unsubstituted C_1-C_{18} alkyl, C_2-C_{18} alkenyl, C_2-C_{18} alkinyl or with halogen, CN, NO_2 or $-COOR_{40}$ substituted or with O or NR_{40} interrupted C_1-C_{18} alkyl, C_2-C_{18} alkenyl or C_2-C_{18} alkinyl;

R_{40} is H, phenyl or C_1-C_{18} alkyl; or

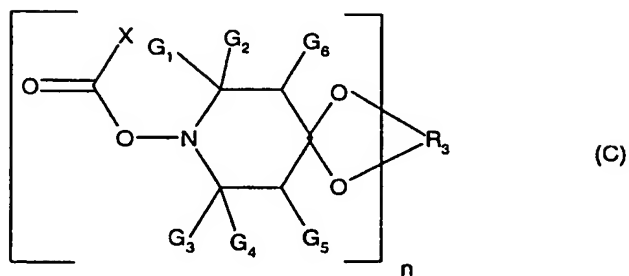
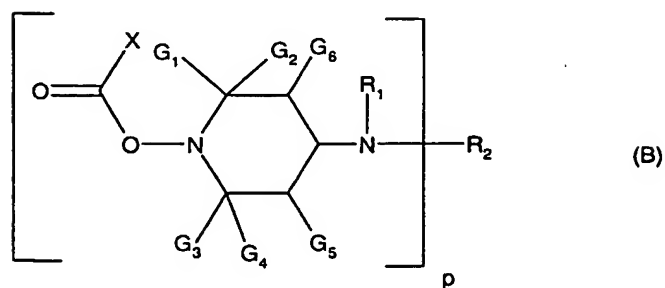
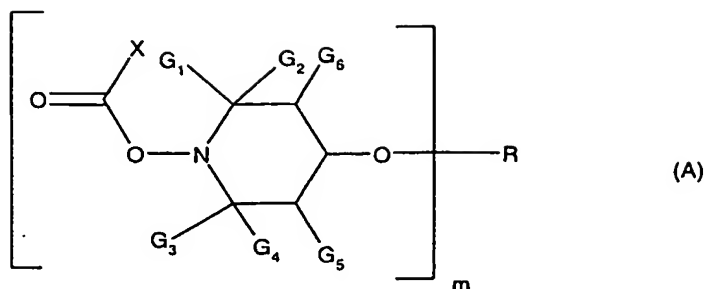
R_{20} and R_{30} together with the nitrogen atom to which they are bound form a 5 or 6 membered ring which may be interrupted by a nitrogen or oxygen atom and which may be substituted by one or more C_1-C_6 alkyl groups, carboxyl groups, C_1-C_{18} alkoxy groups, C_1-C_{18} alkanoyloxy groups.

3. A composition according to claim 1 wherein the structural element of formula (I) is of formula (Ib)



are as defined in claim 1.

4. A composition according to claim 3 wherein the hydroxylamine ester is of formula A, B or C.



wherein

G_1 , G_2 , G_3 and G_4 are methyl or G_1 and G_3 are methyl and G_2 and G_4 are ethyl or G_1 and G_2 are methyl and G_3 and G_4 are ethyl;

G_5 and G_6 are independently hydrogen or methyl;

m is 1;

R is hydrogen, C_1 - C_{18} alkyl which is uninterrupted or C_2 - C_{18} alkyl which is interrupted by one or more oxygen atoms, cyanoethyl, benzoyl, glycidyl, a monovalent radical of an aliphatic carboxylic acid having 2 to 18 carbon atoms, of a cycloaliphatic carboxylic acid having 7 to

15 carbon atoms, or an α,β -unsaturated carboxylic acid having 3 to 5 carbon atoms or of an aromatic carboxylic acid having 7 to 15 carbon atoms, where each carboxylic acid can be substituted in the aliphatic, cycloaliphatic or aromatic moiety by 1 to 3 $-\text{COOZ}_{12}$ groups, in which Z_{12} is H, $\text{C}_1\text{-C}_{20}$ alkyl, $\text{C}_3\text{-C}_{12}$ alkenyl, $\text{C}_5\text{-C}_7$ cycloalkyl, phenyl or benzyl; or

R is a monovalent radical of a carbamic acid or phosphorus-containing acid or a monovalent silyl radical;

p is 1;

R_1 is $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_5\text{-C}_7$ cycloalkyl, $\text{C}_7\text{-C}_8$ aralkyl, $\text{C}_2\text{-C}_{18}$ alkanoyl, $\text{C}_3\text{-C}_5$ alkenoyl or benzoyl;

R_2 is $\text{C}_1\text{-C}_{18}$ alkyl, $\text{C}_5\text{-C}_7$ cycloalkyl, $\text{C}_2\text{-C}_8$ alkenyl unsubstituted or substituted by a cyano, carbonyl or carbamide group, or is glycidyl, a group of the formula $-\text{CH}_2\text{CH}(\text{OH})\text{-Z}$ or of the formula $-\text{CO-Z}$ or $-\text{CONH-Z}$ wherein Z is hydrogen, methyl or phenyl;

n is 1,

R_3 is $\text{C}_2\text{-C}_8$ alkylene or hydroxyalkylene or $\text{C}_4\text{-C}_{36}$ acyloxyalkylene

and

X is hydrogen, $\text{C}_1\text{-C}_{36}$ alkyl or $\text{C}_6\text{-C}_{10}$ aryl.

5. A composition according to claim 4 wherein the hydroxylamine ester is of formula A or C

G_1 , G_2 , G_3 and G_4 are methyl or G_1 and G_3 are methyl and G_2 and G_4 are ethyl;

G_5 and G_6 are independently hydrogen or methyl;

m is 1;

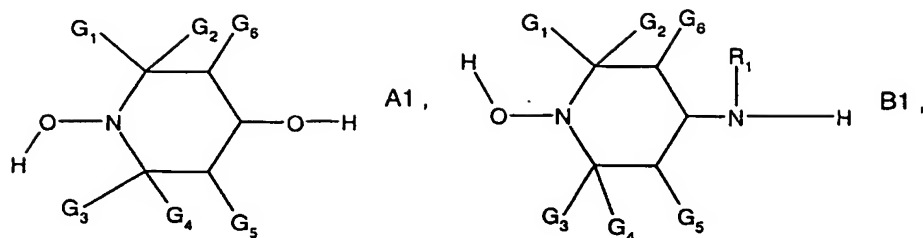
R is hydrogen, $\text{C}_1\text{-C}_{18}$ alkyl, a monovalent radical of an aliphatic carboxylic acid having 2 to 18 carbon atoms, of a cycloaliphatic carboxylic acid having 7 to 15 carbon atoms, or an α,β -unsaturated carboxylic acid having 3 to 5 carbon atoms or of an aromatic carboxylic acid having 7 to 15 carbon atoms;

n is 1;

R_3 is $\text{C}_2\text{-C}_8$ alkylene or hydroxyalkylene or $\text{C}_4\text{-C}_{36}$ acyloxyalkylene and

X is hydrogen, $\text{C}_1\text{-C}_{36}$ alkyl or $\text{C}_6\text{-C}_{10}$ aryl.

6. A composition according to claim 1 wherein the hydroxylamineester is a oligomer or polymer obtainable by reacting a dicarboxylic acid or a dicarboxylic acid derivative with a compound of formula A1 or B1 or by reacting a diisocyanate with a compound of formula A1



wherein the substituents G_1 , G_2 , G_3 , G_4 , G_5 , G_6 and R_1 are as defined in claim 6.

7. A composition according to claim 1 wherein the hydroxylamine ester is present in an amount of from 0.1 to 15 weight-% based on the weight of the polymer.

8. A composition according to claim 1 wherein the polymer substrate is selected from the group of resins consisting of the polyolefins, the thermoplastic olefins, styrenic polymers and copolymers.

9. A composition according to claim 8 wherein the polymer substrate is polypropylene, polyethylene, thermoplastic olefin (TPO), polystyrene, ABS, high impact polystyrene, expandable polystyrene (EPS) and extrusion foamed polystyrene.

10. A composition according to claim 1 wherein the flame retardant component (ii) is selected from the group consisting of

- tetraphenyl resorcinol diphosphite (FYROLFLEX® RDP)
- chloroalkyl phosphate esters (ANTIBLAZE® AB-100 or FYROL® FR-2)
- polybrominated diphenyl oxide (DE-60F)
- decabromodiphenyl oxide (DBDOP),
- antimony trioxide (Sb_2O_3),
- antimony pentoxide (Sb_2O_5),
- tris[3-bromo-2,2-(bromomethyl)propyl] phosphate (PB 370®),
- triphenyl phosphate,
- bis(2,3-dibromopropyl ether) of bisphenol A (PE68),
- ammonium polyphosphate (APP) or (HOSTAFLAM® AP750),
- resorcinol diphosphate oligomer (RDP),
- brominated epoxy resin,

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tetrabromobisphenol A-bis-(allyl ether),
hexabromocyclododecane,
dibromocyclohexane
tribromophenol-cyanurate (Dead Sea® FR-245)
ethylene-bis(tetrabromophthalimide) (BT93),
bis(hexachlorocyclopentadieno)cyclooctane (DECLORANE PLUS®),
calcium sulfate
chlorinated paraffins,
magnesium carbonate,
melamine phosphates,
melamine pyrophosphates,
molybdenum trioxide,
zinc oxide,
1,2-bis(tribromophenoxy)ethane (FF680),
tetrabromo-bisphenol A (SAYTEX® RB100),
Saytex® BC-56HS (Albemarle)
magnesium hydroxide,
alumina trihydrate,
zinc borate, and
ethylenediamine diphosphate (EDAP).
Oligomeric diisopropyl benzene

11. A composition according to claim 10 wherein the flame retardant compound (ii) is tris[3-bromo-2,2-(bromomethyl)propyl] phosphate (PB370), hexabromocyclododecane, tetrabromobisphenol A-bis-(allyl ether), dibromocyclohexane and Saytex BC-56HS (Albemarle).

12. A composition according to claim 1 wherein the flame retardant component (ii) is present in an amount of from 0.1 to 30 weight-% based on the weight of the polymer.

13. A composition according to claim 1 wherein the ratio by weight between component (i) and (ii) is from 10:1 to 1:100.

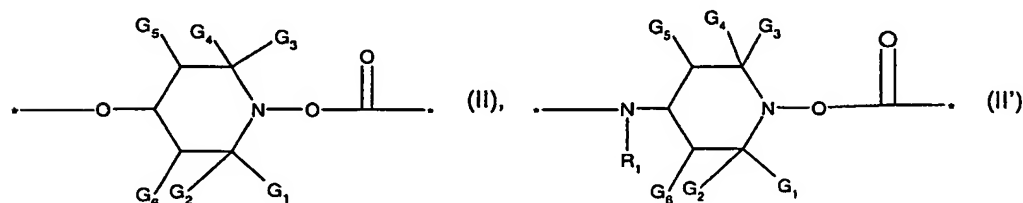
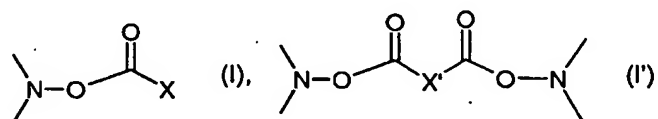
14. A composition according to claim 1, which additionally contains an organic peroxide and/or another radical generator.

15. A composition according to claim 1 which additionally contains a further additive selected from the group consisting of a UV absorber, a sterically hindered amine, a phenolic antioxidant, a phosphite or phosphonite and a benzofuranone or an indolinone.

16. A method of making a thermoplastic polymer flame retarding by incorporating into the thermoplastic polymer

a mixture of

- (i) a hydroxylamine ester having a structural element of formula (I) or formula (I') or with a polymeric hydroxylamine ester having a repetitive structural unit of formula (II) or (II')



wherein

X is hydrogen, C₁-C₃₆alkyl, C₂-C₃₆alkenyl, C₂-C₁₈alkinyl, C₆-C₁₀aryl, -O-C₁-C₁₈alkyl, -O-C₆-C₁₀aryl, -NH-C₁-C₁₈alkyl, -NH-C₆-C₁₀aryl, -N(C₁-C₆alkyl)₂;

X' is a direct bond or C₁-C₃₆alkylene, C₂-C₃₆alkenylene, C₂-C₃₆alkinylene, -(C₁-C₆alkylene)-phenylene-(C₁-C₆alkylene)- or a group from a dimer acid;

G₁, G₂, G₃ and G₄ are independently alkyl of 1 to 4 carbon atoms, or G₁ and G₂ together and G₃ and G₄ together, or G₁ and G₂ together or G₃ and G₄ together are pentamethylene;

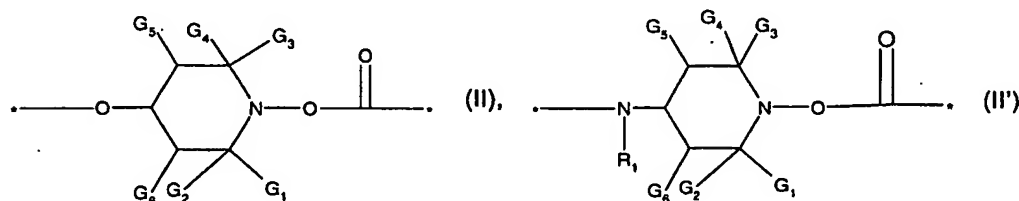
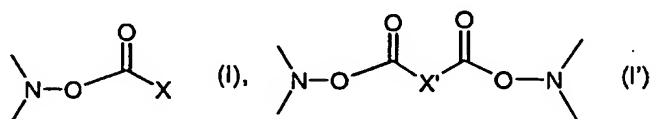
G₅ and G₆ are independently hydrogen or C₁-C₄ alkyl;

R₁ is C₁-C₁₂alkyl, C₅-C₇cycloalkyl, C₇-C₈aralkyl, C₂-C₁₈alkanoyl, C₃-C₅alkenoyl or benzoyl; and

(ii) a flame retardant compound selected from the group consisting of halogenated, phosphorus, boron, silicon and antimony compounds, metal hydroxides, metal hydrates, metal oxides and mixtures thereof.

17. A Flame retardant mixture comprising

- (i) a hydroxylamine ester having a structural element of formula (I) or formula (I') or with a polymeric hydroxylamine ester having a repetitive structural unit of formula (II) or (II')



wherein

X is hydrogen, C₁-C₃₆alkyl, C₂-C₃₆alkenyl, C₂-C₁₈alkinyl, C₆-C₁₀aryl, -O-C₁-C₁₈alkyl, -O-C₆-C₁₀aryl, -NH-C₁-C₁₈alkyl, -NH-C₆-C₁₀aryl, -N(C₁-C₆alkyl)₂;

X' is a direct bond or C₁-C₃₆alkylene, C₂-C₃₆alkenylene, C₂-C₃₆alkynylene, -(C₁-C₆alkylene)-phenylene-(C₁-C₆alkylene) or a group from a dimer acid;

G₁, G₂, G₃ and G₄ are independently alkyl of 1 to 4 carbon atoms, or G₁ and G₂ together and G₃ and G₄ together, or G₁ and G₂ together or G₃ and G₄ together are pentamethylene;

G₅ and G₆ are independently hydrogen or C₁-C₄ alkyl;

R₁ is C₁-C₁₂alkyl, C₅-C₇cycloalkyl, C₇-C₈aralkyl, C₂-C₁₈alkanoyl, C₃-C₅alkenoyl or benzoyl; and

(ii) a flame retardant compound selected from the group consisting of halogenated, phosphorus, boron, silicon and antimony compounds, metal hydroxides, metal hydrates, metal oxides and mixtures thereof.

18. Use of a mixture according to claim 17 as flame retarding additive for thermoplastic polymer articles.

19. Use of a hydroxylaminester according to claim 1 as flame retarding additive for thermoplastic polymer articles.